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Forbidden character in allowed electronic transitions spectra of mono-halonaphthalenes

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The singlet-singlet absorption and emission spectra of α-fluro and the absorption spectra of α-chloro, α-iodo and β-bromo-naphthelenes have been photographed and analysed. The absorption spectra of all the four molecules show the presence of two discrete system of bands and the emission spectrum in case of α-fluoronaphthalene corresponds to the longer wavelength system of absorption.

In case of α-chloro and α-iodo naphthalenes, the longer wavelength system shows the appearance of pure electronic transition with weak bands, while the corresponding transitions in case of α-fluoro and β-bromonaphthalenes appear with the most intense bands of the system as expected theoretically. The appearance of strong vibronic and weak electronic bands in the longer wavelength system of the former two molecules have been interpreted as the interaction of totally symmetric vibrations, a rare example in the literature.

1. INTRODUCTION

Though Albrecht (1960) has shown theoretically, that both symmetric as well as antisymmetric vibrations may act as perturbation in electronic transitions, examples showing the intensification of bands by totally symmetric vibrations are meagre. On the other hand, a number of examples are available in the literature about the effect of non-totally symmetric vibrations. The longer wavelengh ultraviolet system of naphthalene, assigned to $A_g - B_{3u}$ type transition, is an example of the latter type transitions.

On mono-substitution in naphathalene, the symmetry of the molecule changes from D_{2h} to C_s and the non-totally symmetric vibrations of b_{1g} -type responsible for the intensification of bands in the parent hydrocarbon are reduced to totally symmetric a′-type in mono-substituted naphthalenes. According to the principle of allowed transition, the most intense band on the longer wavelength side should be the (0-0) band of each system, but the earlier study of α-bromonaphthalene by us (1975) shows the presence

of stronger vibronic bands than the (0-0) band. In an attempt to understand the electronic spectra of this molecule, we have classified the mono-substituted naphthalenes into two catagories :

(i) The molecule which give rise to strong (0-0) bands were termed as well behaved ones and

(ii) The molecules, like α-bromonaphthalene, which retain the characteristics of the parent molecule, even after the change of the symmetry.

However, if α-bromonaphthalene retains the characteristics of the parent hydrocarbon in the electronic spectra, Raman and I.R. frequencies of this molecule should show the mutual exclusion. A number of confirmatory checks by the authors and the vibrational spectra of this molecule published by Sharma and Singh (1972) and by Michaelian and Ziegler (1973) contradict this point. Taking full account of the above results, we have studied the emission and absorption spectra α-fluoro, and the absorption spectra of α-chloro α-iodo and β-bromonaphthalenes. The study shows that the longer wavelength ultraviolet absorption system of α-chloro, α-bromo and α-iodonaphthalenes is an example of intensification of bands due to the interaction of totally symmetric vibrations.

2. Experimental

The emission spectrum of α-fluoro and the absorption spectra of all the four molecules for higher wavelength system have been photographed in vapour phase using Hilger large quartz (E_1) Spectrograph. Due to the diffuse character of bands the shorter wavelength side of each spectrum could however be photographed on medium quartz spectrograph only. The details of the experimental arrangements are given elsewhere (Singh *et al* 1965). The accuracy of measurements is 2 cm^{-1} in the case of sharp bands and 8 cm^{-1} in the case of diffuse bands.

3. Results

The appearance of bands and their developments at different temperatures indicate very clearly that all the molecules give rise to two systems of discrete absorption The longer wavelength absorption system of α-fluoro, α-chloro, α-iodo and β-bromonaphthalenes has been found to cover the range 3250-2800A while the shorter wavelength is observed in the region 2850-2500A. Hereafter, the longer wavelength will be referred as system I and the shorter one as system II. The emission spectrum of α-fluronaphthalene however, corresponds to absorption system I and covers the region 3600-3100A.

4. Discussion

All the molecules are assigned to C_s -point group with the molecular plane as the only element of symmetry. There are only two types of symmetry species A′ (a′) and A″ (a″), the former being totally symmetric and the latter anitisymmetric with respect to the symmetry operation of reflection in the molecular plane. A comparison of the regions of absorption and the appearance of bands with those of naphthalene indicates that both the systems of absorption in all the molecules, under reference, should be attributed to the allowed transitions of the type $^1A' \leftarrow ^1A'$, with the transition moment along the longer in-plane axis for system I and along the shorter in-plane axis for system II.

Table 1. Pure electronic bands and their shifts from the correspoinding bands of naphthalene

Name of the molecules	System I		System II	
	Position of the (0-0) band (cm^{-1})	Shift from the corresponding band of naphthalene (32020 cm^{-1})	Position of the (0-0) band (cm^{-1})	Shift from the corresponding band of naphthalene (35910 cm^{-1})
α-fluoro-naphthalene	31871	149	35270	640
β-fluoro-* naphthalene	31803	217	36060	−150
α-chloro-naphthalene	31576	444	34801	1109
β-chloro-naphthalene	31422	598	35513	397
α-bromo-naphthalene	31568	452	34607	1303
β-bromo-naphthalene	31411	609	35487	423
α-iodo-naphthalene	31485	535	34481	1429
β-iodo-** naphthalene	31214	806	35154	756

*Frequency from Singh (1975)
**Data from Iredale et al (1960)

In order to satisfy the characteristics of an allowed transition, the most intense band on the longer wavelength side of each system should be taken as the (0-0) band. All the bands shown in table 1 satisfy this characteristic, but for the (0-0) bands in system I of α-chloro, α-bromo and α-iodonaphthalene. In these three cases the weak bands at 31576, 31568 and 31485 cm^{-1} respectively, have been assigned as the (0-0) bands. In the alternative case, when the most intense bands at 32025, 32009 and 31921 cm^{-1} in the three molecules are taken as the (0-0) bands, the intervals 449 and 975 in the case of α-chloro, 441 and 962 cm^{-1} in α-bromo and 436 and 945 in the case of α-iodonaphthalenes should be assigned as ground state frequencies. Since these intervals neither coincide nor show near coincidence in intensity and magnitude with any of the Raman and I.R. frequencies; we prefer the assignment of weak bands as the (0-0) bands.

In the present case the high intensity of bands involving the excited state fundamentals of 449, 441 and 436 cm^{-1} in α-chloro, α-bromo and α-iodonaphthalenes respectively, can be understood on the basis of their correlation with 438 cm^{-1} (b_{1g} -type) excited state frequency of naphthalene. Similar to 438 cm^{-1} excited state frequency of naphthalene, these frequencies also form combinations and the intensity of these combination tones is, in general, more than the fundamental tones. The hot bands at 31050, 31047 and 30973 cm^{-1} in α-chloro, α-bromo and α-iodonaphthalenes respectively, involve the corresponding ground state fundamentals of 526, 521 and 509 cm^{-1} which, in turn, are correlated to 506 cm^{-1} (b_{1g} -type) frequency of naphthalene.

Table 2. Character table for the C_s point group

C_s	E	σ_{xy}		Correspondence with the species of D_{2h}
A′	+	+	T_x, T_y, R_z	A_g, B_{1g}, B_{2u}, B_{3u}
A″	+	−	T_z, R_x, R_y	A_u, B_{1u}, B_{2g}, B_{3g}

On the basis of the correspondence between the symmetry species of D_{2h} and C_s point group, as shown in table 2, the above excited state frequencies may be assigned as totally symmetric vibration of a′—type. The intensification of vibronic bands by totally symmetric vibrations in case of these molecules can be understood on the basis of shifts produced in the electronic bands of parent hydrocarbon by various substitutions. Table 1 reveals that system II is more shifted towards red in case of these three molecules as compared to others. This also shows that the shift of the longer

wavelength system in these molecules is less as compared to the shorter ones. Thus the two electronic states come closer due to the substitution of chlorine, bromine and iodine atoms in the α-position of the parent hydrocarbon. Since both of these electronic states belonging to totally symmetric vibrations of a′—type, the mixing of the electronic eigenfunctions of the two transitions and the intensification of bands are possible (Albrecht 1960 and Herzberg 1966).

Thus, we conclude that the spectra of mono-substituted naphthalenes are of two types. Cases like α-chloro, α-bromo and α-iodonaphthalenes, where a substitution though changes the symmetry of the molecule from D_{2h} to C_s, the characteristic of the electronic spectra are preserved. In other cases like α-fluoronaphthalene and β-substituted compounds, the characteristics of the electronic spectra of naphthalene are changed completely. The former class of molecules provide an example of intensification of bands by totally symmetric vibrations.

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REFERENCES

Albrecht, A. C 1960 J. Chem. Phys, **33,** 156

Singh, S N, Sharma, O. P. & Singh R. D. 1975 Spectroscopy Letter, **8,** 7.

Sharma, O. P. & Singh, R. D. 1972 Ind. J Pure & Appl. Phys, **10,** 885.

Michaelian, K. H. & Ziegler, S. M. 1973 Appl. Spectroscopy, **27,** 13.

Singh, R. D. & Singh R. S 2965 Ind. J Pure & Appl. Phys., **3,** 418

Herzberg, G. 1966 Molecular Spectra and Molecular Structure Vol. III (D. Van Nostrand Company, Inc)

Singh, R. D 1975 Ind. J Pure & Appl. Phys. **13,** 48

Iredale, T. & White, J. W. 1960 Trans Faraday Soc, **56,** 1719.